Group Vector Space (GVS) Method for Estimating Boiling and Melting Points of Hydrocarbons

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The specific position of the group in the molecule has been considered, and a group vector space (GVS) method for estimating boiling and melting points of hydrocarbons has been proposed. Expressions for boiling point T_b and melting point T_m have been proposed, with the numerical values of relative group parameters presented. The average percent deviations of estimation of the T_b and T_m values are 1.05 and 7.96, respectively.

Introduction

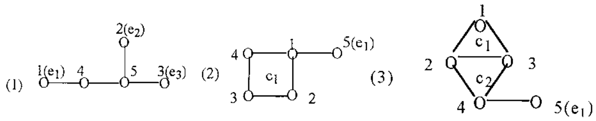
Melting and boiling points of hydrocarbons are basic physical property data, and they are applied widely in domains such as state calculation, process simulation, and product design. However, it is not always possible to find reliable experimental values of melting and boiling points for the compounds of interest, nor is it practical to measure the properties as the need arises. So the estimation of melting and boiling points is required.

For the estimation of properties of pure compounds, simple group contribution methods[1−5] are widely used. These methods provide the important advantage of quick estimates without requiring substantial computational resources. However, many of these methods are of questionable accuracy and utility. To overcome this limitation, complex group contribution methods have been reported in the literature. Two representatives of them are the two-level group contribution method by Constantinou and Gani[6] and the group-interaction contribution (GIC) method by Marrero-Morejon and Pardillo-Fontdevila.[7] But there exists another problem about complex group contribution methods. For the Constantinou and Gani method, the estimation is performed at two levels: the basic level uses the contribution from first-order groups, while the second level increases the consideration of the second-order groups. Their 78 first-order groups are not sufficient to describe the molecules of some common compounds, and under certain circumstances the same molecule may be described in different ways because of overcomplication of this method. For the GIC method, the number of parameters in the property correlation is 223, which has no very large difference from the number of substances in the regression. As we known, only if the number of substances in the linear data regression is much more than that of parameters in the model, the group method has a function of extrapolation predicting.

In this paper, consideration of the group position in the molecule will be increased starting from the property estimation for hydrocarbons, and a new method for estimating physical properties to limit the number of model parameters with higher accuracy will be proposed.

Group Vector Space for Hydrocarbons

In this work, we select 15 simple groups to describe hydrocarbons. These groups are the same as those used by Joback and Reid.[1] The molecule is considered to be in a given space, and every group in the molecule is only a point in the space. The molecules of hydrocarbons can be divided into three kinds: chain molecule, monocyclic molecule, and polycyclic molecule. To write them conveniently, graphs with different numbers of points are all expressed as graphs with five points. Thus, the hydrocarbon molecules can be expressed as the following three topologic graphs:



Considering the chain graph first, the dimension number of the space is equal to the number of end points (e_i) on the chain, and one end point has determined a dimension of the space. The coordinate of an end point in the dimension determined by it is zero, while the coordinate of another point in this dimension is the distance from that point to the end point. For the cyclic graph, one ring (c_i) represents a dimension. In that dimension the coordinate of the ring point equals the number of points on the ring, and the coordinate of the nonring point equals the sum of the distance from that point to the ring and the number of points on the ring. If the route from the ring point to the end point is nonunique, the shortest route should be selected. So the dimension number m of the space for a graph is equal to the sum of the number k_e of end points (e_i) and the number k_c of rings (c_i) in the graph. Every point in the graph has m coordinates in the m-dimension space. The graph may be described by a space matrix, the number of rows in the matrix equals the number of points in the graph, and the number of columns equals the dimension number of the space. The space matrices of the above three topologic graphs are as follows:

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Table 1. Values of Group Parameters

		T_b/K			T_m/K		
group serial no.	group	ΔT_{bpi} ($\times 10^{-3}$)	ΔT_{bIi} ($\times 10^{-3}$)	ΔT_{b0i} ($\times 10^{-3}$)	ΔT_{mpi}	ΔT_{mIi}	ΔT_{m0i}
1	$-CH_3$	28.014	0.382	4.002	16.807	11.978	−14.989
2	$>CH_2$	26.538	15.469	−3.713	49.834	3.528	−23.524
3	$>CH-$	−37.025	43.225	−1.202	121.446	−29.489	−6.232
4	$>C<$	−70.493	63.161	−6.596	−162.560	98.998	−54.509
5	$=CH_2$	15.734	7.786	−3.865	−28.851	26.481	3.324
6	$=CH-$	23.652	15.470	−0.148	64.137	−9.825	−5.122
7	$=C<$	−7.432	40.597	−3.584	160.354	−6.304	−29.431
8	$=C=$	64.421	0.644	6.070	258.714	−7.767	−63.212
9	$\equiv CH$	−1.465	32.376	−17.653	−17.230	52.837	16.228
10	$\equiv C-$	49.124	17.246	−10.876	92.108	34.406	−70.901
11	$(>CH_2)_R$[a]	14.811	18.849	−9.119	26.999	13.608	−9.800
12	$(>CH-)_R$	−15.089	34.127	−4.594	−75.346	36.862	−30.944
13	$(>C<)_R$	−180.914	107.266	−20.330	−614.110	251.005	−20.573
14	$(=CH-)_R$	47.022	7.379	−10.373	59.601	6.461	−29.994
15	$(=C<)_R$	−1.375	41.495	−8.037	37.857	29.595	−49.134

[a] R represents the group on the ring.

$$\begin{array}{c|ccc} & e_1 & e_2 & e_3 \\ \hline 1 & 0 & 3 & 3 \\ 2 & 3 & 0 & 2 \\ 3 & 3 & 2 & 0 \\ 4 & 1 & 2 & 2 \\ 5 & 2 & 1 & 1 \end{array} \tag{1}$$

$$\begin{array}{c|cc} & c_1 & e_1 \\ \hline 1 & 4 & 1 \\ 2 & 4 & 2 \\ 3 & 4 & 3 \\ 4 & 4 & 2 \\ 5 & 5 & 0 \end{array} \tag{2}$$

$$\begin{array}{c|ccc} & c_1 & c_2 & e_1 \\ \hline 1 & 3 & 4 & 3 \\ 2 & 3 & 3 & 2 \\ 3 & 3 & 3 & 2 \\ 4 & 4 & 3 & 1 \\ 5 & 5 & 4 & 0 \end{array} \tag{3}$$

The matrices show that the space position of point i in the graph can be represented by an m-dimensional vector ($b_{i1}\ b_{i2}\ ...\ b_{im}$). Then the module a_i of the point i vector is

$$\alpha_i = (\sum_{j=1}^{m} b_{ij}^{\,2})^{1/2} \quad (i = 1, 2, 3, 4, 5)$$

The average square root of the module of some point i in the graph is defined as the module index ν_i of this point vector. That is

$$\nu_i = \alpha_i / (\sum_{j=1}^{5} \alpha_j^{\,2})^{1/2} \quad (i = 1, 2, 3, 4, 5)$$

The quantity ν_i is used to describe the point i position in the space. In analogy to this, the module index ν_i of group i in the molecule is taken to characterize the position of that group in the molecular space. Thus, every simple group in the molecule has its own independent module index.

Table 2. Average Estimation Deviations of Melting and Boiling Points by the Group Vector Space Method and the Traditional Simple Group Contribution Method

		percent deviation/%		absolute deviation/K	
property	no. of compound	eq 1	eq 2	eq 1	eq 2
T_m	339	12.86	7.96	26.22	16.77
T_b	402	2.50	1.24	9.66	5.09

Correlation and Group Parameters

The expression of physical property f for the simple group method is

$$f = a + \sum_i n_i \Delta f_i \tag{1}$$

where subscript i represents the group type, Δf_i is the contribution value of the i-type group, n_i is the number of i-type groups in the molecule, and a is the correlation constant.

In this study, the group contribution was divided into two parts: the position contribution of the group and the independent contribution of the group. The physical property f is expressed as follows:

$$f = a + \sum_i (\sum_{j=1}^{n_i} \nu_j \Delta f_{Pi} + n_i \Delta f_{Ii} + \Delta f_{0i}) \tag{2}$$

where Δf_{Pi} is the position contribution of the i-type group, Δf_{Ii} is the independent contribution of the i-type group, Δf_{0i} is the constant of the i-type group, and $\sum_{j=1}^{n_i} \nu_j$ is the module index sum of i-type groups.

To improve the property estimation accuracy, the power index “1”of property f in eq 2 is substituted by a variable, the optimum value of which can be obtained by a trial computation. Upon doing this, the expressions of T_m and T_b may be written as follows:

$$T_m = 72.42 + \sum_i (\sum_{j=1}^{n_i} \nu_j \Delta T_{mPi} + n_i \Delta T_{mIi} + \Delta T_{m0i}) \tag{3}$$

$$T_b^{\,2.0} = -10157.64 + \sum_i (\sum_{j=1}^{n_i} \nu_j \Delta T_{bPi} + n_i \Delta T_{bIi} + \Delta T_{b0i}) \tag{4}$$

Table 3. Average Estimation Deviations of T_b and T_m for Four Groups of Hydrocarbons

	T_b/K			T_m/K		
compound	no. of data points	absolute deviation	percent deviation/%	no. of data points	absolute deviation	percent deviation/%
alkanes	92	2.785	0.709	67	14.83	7.929
alkenes/alkynes	120	3.011	0.961	102	11.53	7.029
cyclic	110	4.270	1.114	92	15.13	7.852
aromatic	80	7.540	1.500	78	27.212	9.352
total	402	4.205	1.052	339	16.769	7.965

Table 4. Comparison of Prediction Results between This Method and the JR Method

	percent deviation of T_b/K, %		percent deviation of T_m/K, %	
compoud	this method	JR method	this method	JR method
2-methylbutane	−0.829	4.378	6.77	15.34
2,6-dimethylheptane	−0.754	−0.705	−0.160	−5.576
isobutylene	0.869	8.175	−0.986	−10.68
2-hexyne	−0.005	−3.207	−0.124	43.17
n-butylcyclopentane	0.0136	−2.071	7.036	22.04
1,1,2-trimethylcyclohexane	−0.082	−0.681	−3.545	−10.77
isopropylbenzene	1.044	1.536	6.80	14.10
diphenyl	−2.357	−0.167	−8.85	−18.95
average	0.744	2.615	4.284	17.58

where T_m and T_b are the melting point and the boiling point, respectively, and the units employed are all Kelvin.

A great deal of the experimental data in the literature[8−10] have been used to optimize the values of the group parameters in eqs 3 and 4, which are shown in Table 1.

Method Comparison and Estimation Results

The group division in this work is the same as that of the Joback and Reid method.[1] The Joback and Reid method is a traditional simple group contribution method, which is suitably expressed by eq 1. The results of a comparison between eqs 1 and 2 are listed in Table 2.

The boiling points of the 402 compounds and the melting points of the 339 compounds are divided into four groups, and the average deviations between the values calculated by this method and the experimental data of each group are listed in Table 3.

The predictions of T_b and T_m by the new method are compared with that by the Joback and Reid (JR) method[1] in Table 4, where eight compounds are chosen for comparison randomly.

From Tables 2 and 4, it can be seen that the new method presented gave more accurate predictions of T_b and T_m of hydrocarbons than the traditional simple group contribution method. Table 3 shows that the proposed method can give better predictions of T_b and T_m of hydrocarbons.

Conclusion

The specific position of a group in the molecule has been considered, and a group vector space (GVS) method for estimating melting and boiling points of hydrocarbons has been proposed. Expressions for T_m and T_b have been proposed, with the numerical values of relative group parameters presented. The average percent deviations of estimation of T_m and T_b are 1.05 and 7.96, respectively, which show that the present method is a successful method for estimating melting and boiling points of hydrocarbons.

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